10-24-00

A

Practitioner's Docket No. 1012-065D1 *PATENT*

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Box Patent Application
Assistant Commissioner for Patents
Washington, D.C. 20231

NEW APPLICATION TRANSMITTAL

Transmitted herewith for filing is the patent application of
Inventor(s): Christopher J. Warren; Robert C. Haushalter, Leonid Matsiev

WARNING: *37 C.F.R. Section 1.41(a)(1) points out:*

"(a) A patent is applied for in the name or names of the actual inventor or inventors.

(1) The inventorship of a nonprovisional application is that inventorship set forth in the oath or declaration

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CERTIFICATION UNDER 37 C.F.R. SECTIONS 1.8(a) AND 1.10*
*(When using Express Mail, the Express Mail label number is **mandatory**;*
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

MAILING

[X] deposited with the United States Postal Service in an envelope addressed to Box Patent Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

37 C.F.R. Section 1.8(a)

[ ] with sufficient postage as first class mail.

37 C.F.R. Section 1.10*

[X] as "Express Mail Post Office to Address" Mailing Label No. EL564195246US

TRANSMISSION

[ ] transmitted by facsimile to the Patent and Trademark Office (703) ____-____

Date: 10/23/00

Enid Wasserman

Signature Enid Wasserman

(*type or print name of person certifying*)

***WARNING:** *Each paper or fee filed by "Express Mail" **must** have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. Section 1.10(b).*
*"Since the filing of correspondence under [Section] 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will **not** be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.*

as prescribed by Section 1.63, except as provided for in Section 1.53(d)(4) and Section 1.63(d). If an oath or declaration as prescribed by Section 1.63 is not filed during the pendency of a nonprovisional application, the inventorship is that inventorship set forth in the application papers filed pursuant to Section 1.53(b), unless a petition under this paragraph accompanied by the fee set forth in Section 1.17(I) is filed supplying or changing the name or names of the inventor or inventors."

For (title): COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND TESTING SYSTEM

1. Type of Application

This new application is for a(n)

(check one applicable item below)

[X] Original (nonprovisional)
[ ] Design
[ ] Plant

WARNING: ***Do not*** *use this transmittal for a completion in the U.S. of an International Application under 35 U.S.C. 371(c)(4), unless the International Application is being filed as a divisional, continuation or continuation-in-part application.*

WARNING: ***Do not*** *use this transmittal for the filing of a provisional application.*

NOTE: If one of the following 3 items apply, then complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U.S. APPLICATION CLAIMED and a NOTIFICATION IN PARENT APPLICATION OF THE FILING OF THIS CONTINUATION APPLICATION.

[X] Divisional.
[ ] Continuation.
[ ] Continuation-in-part (C-I-P).

2. Benefit of Prior U.S. Application(s) (35 U.S.C. Sections 119(e), 120, or 121)

NOTE: A nonprovisional application may claim an invention disclosed in one or more prior filed copending nonprovisional applications or copending international applications designating the United States of America. In order for a nonprovisional application to claim the benefit of a prior filed copending nonprovisional application or copending international application designating the United States of America, each prior application must name as an inventor at least one inventor named in the later filed nonprovisional application and disclose the named inventor's invention claimed in at least one claim of the later filed nonprovisional application in the manner provided by the first paragraph of 35 U.S.C. Section 112. Each prior application must also be:

(I) An international application entitled to a filing date in accordance with PCT Article 11 and designating the United States of America; or

(ii) Complete as set forth in Section 1.51(b); or

(iii) Entitled to a filing date as set forth in Section 1.53(b) or Section 1.53(d) and include the basic filing fee set forth in Section 1.16; or

(iv) Entitled to a filing date as set forth in Section 1.53(b) and have paid therein the processing and retention fee set forth in Section 1.21(l) within the time period set forth in Section 1.53(f).

37 C.F.R. Section 1.78(a)(1).

NOTE *If the new application being transmitted is a divisional, continuation or a continuation-in-part of a parent case, or where the parent case is an International Application which designated the U.S., or benefit of a prior provisional application is claimed, then check the following item and complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.*

WARNING: *If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. 120, 121 or 365(c). (35 U.S.C. 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. 119, 365(a) or 365(b).) For a c-I-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.*

WARNING: *When the last day of pendency of a provisional application falls on a Saturday, Sunday, or Federal holiday within the District of Columbia, any nonprovisional application claiming benefit of the provisional application* ***must*** *be filed prior to the Saturday, Sunday, or Federal holiday within the District of Columbia. See 37 C.F.R. Section 1.78(a)(3).*

[X] The new application being transmitted claims the benefit of prior U.S. application(s). Enclosed are ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

3. Papers Enclosed

A. Required for Filing Date under 37 C.F.R. Section 1.53(b) (Regular) or 37 C.F.R. Section 1.153 (Design) Application

14 Pages of Specification
7 Pages of Claims
8 Sheets of Drawing (as originally filed)

WARNING: ***DO NOT*** *submit original drawings. A high quality copy of the drawings should be supplied when filing a patent application. The drawings that are submitted to the Office must be on strong, white, smooth, and non-shiny paper and meet the standards according to Section 1.84. If corrections to the drawings are necessary, they should be made to the original drawing and a high-quality copy of the corrected original drawing then submitted to the Office. Only one copy is required or desired. For comments on proposed then-new 37 C.F.R. 1.84, see Notice of March 9, 1988 . (1990 O.G. 57-62).*

NOTE: *"Identifying indicia, if provided, should include the application number or the title of the invention, inventor's name, docket number (if any), and the name and telephone number of a person to call if the Office is unable to match the drawings to the proper application. This information should be placed on the back of each sheet of drawing a minimum distance of 1.5 cm. (5/8 inch) down from the top of the page. . ." 37 C.F.R. Section 1.84(c)).*

(complete the following, if applicable)

[ ] The enclosed drawing(s) are photograph(s), and there is also attached a "PETITION TO ACCEPT PHOTOGRAPH(S) AS DRAWING(S)." 37 C.F.R. Section 1.84(b).

[X] Formal Drawings as filed on January 28, 2000 in parent application (6 sheets)
[ ] Informal

B. Other Papers Enclosed

2 Pages of declaration and power of attorney
1 Pages of Abstract
2 Other: Certificate Under 37 CFR 3.73(b) and Power of Attorney by Assignee

4. Additional Papers Enclosed

[X] Amendment to claims

[X] Cancel in this applications claims 1-29 and 35-37 before calculating the filing fee. (At least one original independent claim must be retained for filing purposes.)
[] Add the claims shown on the attached amendment. (Claims added have been numbered consecutively following the highest numbered original claims.)

[X] Preliminary Amendment
[ ] Information Disclosure Statement (37 C.F.R. Section 1.98)
[ ] Form PTO-1449 (PTO/SB/08A and 08B)
[ ] Citations
[ ] Declaration of Biological Deposit
[ ] Submission of "Sequence Listing," computer readable copy and/or amendment pertaining thereto for biotechnology invention containing nucleotide and/or amino acid sequence.
[ ] Authorization of Attorney(s) to Accept and Follow Instructions from Representative
[ ] Special Comments
[ ] Other

5. Declaration or Oath (including power of attorney)

NOTE: A newly executed declaration is not required in a continuation or divisional application provided the prior nonprovisional application contained a declaration as required, the application being filed is by all or fewer than all the inventors named in the prior application, there is no new matter in the application being filed, and a copy of the executed declaration filed in the prior application (showing the signature or an indication thereon that it was signed) is submitted. The copy must be accompanied by a statement requesting deletion of the names of person(s) who are not inventors of the application being filed. If the declaration in the prior application was filed under Section 1.47 then a copy of that declaration must be filed accompanied by a copy of the decision granting Section 1.47 status or, if a nonsigning person under Section 1.47 has subsequently joined in a prior application, then a copy of the subsequently executed declaration must be filed. See 37 C.F.R. Section 1.63(d)(1)-(3).

NOTE: A declaration filed to complete an application must be executed, identify the specification to which it is directed, identify each inventor by full name, including the family name, and at least one given name without abbreviation

together with any other given name or initial, and the residence, post office address and country of citizenship of each inventor, and state whether the inventor is a sole or joint inventor. 37 C.F.R. Section 1.63(a)(1)-(4).

NOTE: A The inventorship of a nonprovisional application is that inventorship set forth in the oath or declaration as prescribed by Section 1.62, except as provided for in Section 1.53(d)(4) and Section 1.63(d). If an oath or declaration as prescribed by Section 1.63 is not filed during the pendency of a nonprovisional application, the inventorship is that inventorship set forth in the application papers filed pursuant to Section 1.53(b), unless a petition under this paragraph accompanied by the fee set forth in Section 1.17(I) is filed supplying or changing the name or names of the inventor or inventors. 37 C.F.R. Section 1.41(a)(1).

[X] Enclosed

Executed by

(check **all** *applicable boxes)*

[X] inventor(s).
[ ] legal representative of inventor(s). 37 C.F.R. Section 1.42 or 1.43.
[ ] joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.

[ ] This is the petition required by 37 C.F.R. Section 1.47 and the statement required by 37 C.F.R. Section 1.47 is also attached. See item 13 below for fee.

[ ] Not Enclosed.

NOTE: *Where the filing is a completion in the U.S. of an International Application, or where the completion of the U.S. application contains subject matter in addition to the International Application, the application may be treated as a continuation or continuation-in-part, as the case may be, utilizing ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION CLAIMED.*

[ ] Application is made by a person authorized under 37 C.F.R. 1.41 on behalf of *all* the above named inventor(s).

(The declaration or oath, along with the surcharge required by 37 C.F.R. Section 1.16(e), can be filed subsequently).

[ ] Showing that the filing is authorized.
(not required unless called into question. 37 C.F.R. Section 1.41(d))

6. Inventorship Statement

WARNING: *If the named inventors are each not the inventors of all the claims an explanation, including the ownership of the various claims at the time the last claimed invention was made, should be submitted.*

The inventorship for all the claims in this application are:

[X] The same.

or

[ ] Not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made,

[ ] is submitted.

[ ] will be submitted.

7. Language

NOTE: An application including a signed oath or declaration may be filed in a language other than English. An English translation of the non-English language application and the processing fee of $130.00 required by 37 C.F.R. Section 1.17(k) is required to be filed with the application, or within such time as may be set by the Office. 37 C.F.R. Section 1.52(d).

[X] English

[ ] Non-English

[ ] The attached translation includes a statement that the translation is accurate. 37 C.F.R. Section 1.52(d).

8. Assignment

[X] An assignment of the invention to Symyx Technologies, Inc. was recorded in the parent application in reel/frame 9340/0109 on July 20, 1998. (Copy attached)

[ ] is attached. A separate [ ] "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or [ ] FORM PTO 1595 is also attached.

[ ] will follow.

NOTE: "If an assignment is submitted with a new application, send two separate letters-one for the application and one for the assignment" Notice of May 4, 1990 (1114 O.G. 77-78).

WARNING: *A newly executed "STATEMENT UNDER 37 C.F.R. Section 3.73(b)" must be filed when a continuation-in-part application is filed by an assignee. Notice of April 30, 1993, 1150 O.G. 62-64.*

9. Certified Copy

Certified copy(ies) of application(s)

Country	Appln. no.	Filed
Country	Appln. no.	Filed

Country	Appln. no.	Filed

from which priority is claimed

[ ] is (are) attached.
[ ] will follow.

NOTE: The foreign application forming the basis for the claim for priority must be referred to in the oath or declaration. 37 C.F.R. Section 1.55(a) and 1.63.

NOTE: This item is for any foreign priority for which the application being filed directly relates. If any parent U.S. application or International Application from which this application claims benefit under 35 U.S.C. 120 is itself entitled to priority from a prior foreign application, then complete item 18 on the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

10. Fee Calculation (37 C.F.R. Section 1.16)

A. [X] Regular application

CLAIMS AS FILED

Claims	Number Filed	Basic Fee Allowance	Number Extra	Rate	Basic Fee 37 C.F.R. Section 1.16(a) $710.00
Total Claims (37 C.F.R. Section 1.16(c))	5	- 20 =	x	$ 18.00	
Independent Claims (37 C.F.R. Section 1.16(b))	2	- 3 =	x	$ 80.00	
Multiple Dependent Claim(s), if any (37 C.F.R. Section 1.16(d))			+	$260.00	

[ ] Amendment cancelling extra claims is enclosed.
[ ] Amendment deleting multiple-dependencies is enclosed.
[ ] Fee for extra claims is not being paid at this time.

NOTE: If the fees for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency. 37 C.F.R. Section 1.16(d).

Filing Fee Calculation $_____

B. [ ] Design application
($310.00--37 C.F.R. Section 1.16(f))
Filing Fee Calculation $_____

C. [ ] Plant application
($480.00--37 C.F.R. Section 1.16(g))
Filing Fee Calculation $_____

11. Small Entity Statement(s)

[ ] Statement(s) that this is a filing by a small entity under 37 C.F.R. Section 1.9 and 1.27 is (are) attached.

WARNING: *"Status as a small entity must be specifically established in each application or patent in which the status is available and desired. Status as a small entity in one application or patent does not affect any other application or patent, including applications or patents which are directly or indirectly dependent upon the application or patent in which the status has been established. The refiling of an application under Section 1.53 as a continuation, division, or continuation-in-part (including a continued prosecution application under Section 1.53(d)), or the filing of a reissue application requires a new determination as to continued entitlement to small entity status for the continuing or reissue application. A nonprovisional application claiming benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) of a prior application, or a reissue application may rely on a statement filed in the prior application or in the patent if the nonprovisional application or the reissue application includes a reference to the statement in the prior application or in the patent or includes a copy of the statement in the prior application or in the patent and status as a small entity is still proper and desired. The payment of the small entity basic statutory filing fee will be treated as such a reference for purposes of this Section." 37 C.F.R. Section 1.28(a)(2).*

WARNING: *"Small entity status must not be established when the person or persons signing the . . . statement can **unequivocally** make the required self-certification." M.P.E.P. Section 509.03, 6th ed., rev. 2, July 1996 (emphasis added).*

(complete the following, if applicable)

[X] Status as a small entity was claimed in prior application 09/119,187, filed on July 20, 1998 from which benefit is being claimed for this application under:

35 U.S.C. Section	[ ]	119(e),
	[ ]	120,
	[X]	121,
	[ ]	365(c),

and which status as a small entity is still proper and desired.

[X] A copy of the statement in the prior application is included.

Filing Fee Calculation (50% of **A**, **B** or **C** above) $355.00

NOTE: Any excess of the full fee paid will be refunded if a small entity status is established refund request are filed within 2 months of the date of timely payment of a full fee. The two-month period is not extendable under Section 1.136. 37 C.F.R. Section 1.28(a).

12. Request for International-Type Search (37 C.F.R. Section 1.104(d))

(complete, if applicable)

[ ] Please prepare an international-type search report for this application at the time when national examination on the merits takes place.

13. Fee Payment Being Made at This Time

[ ] Not Enclosed

[ ] No filing fee is to be paid at this time.
(This and the surcharge required by 37 C.F.R. Section 1.16(e) can be paid subsequently.)

[X] Enclosed

[X] Filing fee $355.00

[ ] Recording assignment
($40.00; 37 C.F.R. Section 1.21(h))
(See attached "COVER SHEET FOR ASSIGNMENT ACCOMPANYING NEW APPLICATION.") $_____

[ ] Petition fee for filing by other than all the inventors or person on behalf of the inventor where inventor refused to sign or cannot be reached
($130.00; 37 C.F.R. Sections 1.47 and 1.17(I))$__

[ ] For processing an application with a specification in a non-English language
($130.00; 37 C.F.R. Sections 1.52(d) and 1.17(k)) $_____

Practitioner's Docket No. 1012-065D1 *PATENT*

ADDED PAGES FOR APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED

NOTE: See 37 C.F.R. Section 1.78.

17. Relate Back

WARNING: *If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. Section 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. Section 120, 121 or 365(c). (35 U.S.C. Section 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. Section 119, 365(a) or 365(b).) For a c-I-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.*

(complete the following, if applicable)

[X] Amend the specification by inserting, before the first line, the following sentence:

A. 35 U.S.C. Section 119(e)

NOTE: "Any nonprovisional application claiming the benefit of one or more prior filed copending provisional applications must contain or be amended to contain in the first sentence of the specification following the title a reference to each such prior provisional application, identifying it as a provisional application, and including the provisional application number (consisting of series code and serial number)." 37 C.F.R. Section 1.78(a)(4).

[ ] "This application claims the benefit of U.S. Provisional Application(s) No(s).:

APPLICATION NO(S).:	**FILING DATE**
_____ /_____	_____"
_____ /_____	_____"
_____ /_____	_____"

B. 35 U.S.C. Sections 120, 121 and 365(c)

NOTE: "Except for a continued prosecution application filed under Section 1.53(d), any nonprovisional application claiming the benefit of one or more prior filed copending nonprovisional applications or international applications designating the United States of America must contain or be amended to contain in the first sentence of the specification following the title a reference to each such prior application, identifying it by application number (consisting of the series code and serial number) or international application number and international filing date and indicating the relationship of the applications. . . . Cross-references to other related applications may be made when appropriate." (See Section 1.14(a)). 37 C.F.R. Section 1.78(a)(2).

[X] "This application is a

[ ] continuation

[ ] continuation-in-part

[X] divisional

of copending application(s)

[X] application number 09/119,187 filed on July 20, 1998, which is a continuation in part of 08/941,170, filed September 30, 1997."

[ ] International Application _____ filed on _____ and which designated the U.S."

NOTE: The proper reference to a prior filed PCT application that entered the U.S. national phase is the U.S. serial number and the filing date of the PCT application that designated the U.S.

NOTE: (1) Where the application being transmitted adds subject matter to the International Application, then the filing can be as a continuation-in-part or (2) if it is desired to do so for other reasons then the filing can be as a continuation.

NOTE: The deadline for entering the national phase in the U.S. for an international application was clarified in the Notice of April 28, 1987 (1079 O.G. 32 to 46) as follows:

"The Patent and Trademark Office considers the International application to be pending until the 22nd month from the priority date if the United States has been designated and no Demand for International Preliminary Examination has been filed prior to the expiration of the 19th month from the priority date and until the 32nd month from the priority date if a Demand for International Preliminary Examination which elected the United States of America has been filed prior to the expiration of the 19th month from the priority date, provided that a copy of the international application has been communicated to the Patent and Trademark Office within the 20 or 30 month period respectively. If a copy of the international application has not been communicated to the Patent and Trademark Office within the 20 or 30 month period respectively, the international application becomes abandoned as to the United States 20 or 30 months from the priority date respectively. These periods have been placed in the rules as paragraph (h) of Section 1.494 and paragraph (I) of Section 1.495. A continuing application under 35 U.S.C. 365(c) and 120 may be filed anytime during the pendency of the international application."

[ ] "The nonprovisional application designated above, namely application _____/_____, filed _____, claims the benefit of U.S. Provisional Application(s) No(s).:

APPLICATION NO(S).:	**FILING DATE**
_____/_____	_____"
_____/_____	_____"
_____/_____	_____"

[ ] Where more than one reference is made above please combine all references into one sentence.

18. Relate Back--35 U.S.C. Section 119 Priority Claim for Prior Application

The prior U.S. application(s), including any prior International Application designating the U.S., identified above in item 17B, in turn itself claim(s) foreign priority(ies) as follows:

Country	Appln. no.	Filed

The certified copy(ies) has (have)

[ ] been filed on _____, in prior application 0 /_____, which was filed on _____.

[ ] is (are) attached.

WARNING: The certified copy of the priority application that may have been communicated to the PTO by the International Bureau may not be relied on without any need to file a certified copy of the priority application in the continuing application. This is so because the certified copy of the priority application communicated by the International Bureau is placed in a folder and is not assigned a U.S. serial number unless the national stage is entered. Such folders are disposed of if the national stage is not entered. Therefore, such certified copies may not be available if needed later in the prosecution of a continuing application. An alternative would be to physically remove the priority documents from the folders and transfer them to the continuing application. The resources required to request transfer, retrieve the folders, make suitable record notations, transfer the certified copies, enter and make a record of such copies in the Continuing Application are substantial. Accordingly, the priority documents in folders of international applications that have not entered the national stage may not be relied on. Notice of April 28, 1987 (1079 O.G. 32 to 46).

19. Maintenance of Copendency of Prior Application

NOTE: The PTO finds it useful if a copy of the petition filed in the prior application extending the term for response is filed with the papers constituting the filing of the continuation application. Notice of November 5, 1985 (1060 O.G. 27).

A. [ ] Extension of time in prior application

*(This item **must** be completed and the papers filed **in the prior application,** if the period set in the prior application has run.)*

[ ] A petition, fee and response extends the term in the pending **prior** application until _____

[ ] A **copy** of the petition filed in prior application is attached.

B. [ ] Conditional Petition for Extension of Time in Prior Application

(complete this item, if previous item not applicable)

[ ] A conditional petition for extension of time is being filed in the pending **prior** application.

[ ] **A copy** of the conditional petition filed in the prior application is attached.

20. Further Inventorship Statement Where Benefit of Prior Application(s) Claimed

(complete applicable item (a), (b) and/or (c) below)

(a) [X] This application discloses and claims only subject matter disclosed in the prior application whose particulars are set out above and the inventor(s) in this application are believed to be the same.

[X] In view of correction of inventorship being effected in the prior application, inventorship is being investigated in the present application. In the event correction is deemed necessary, Applicants will submit an appropriate request for correction.

[ ] less than those named in the prior application. It is requested that the following inventor(s) identified for the prior application be deleted:

_____

(type name(s) of inventor(s) to be deleted)

(b) [ ] This application discloses and claims additional disclosure by amendment and a new declaration or oath is being filed. With respect to the prior application, the inventor(s) in this application are

[ ] the same.

[ ] the following additional inventor(s) have been added:

_____

(type name(s) of inventor(s) to be deleted)

(c) [ ] The inventorship for all the claims in this application are

[ ] the same.

[ ] not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made

[ ] is submitted.

[ ] will be submitted.

21. Abandonment of Prior Application *(if applicable)*

[ ] Please abandon the prior application at a time while the prior application is pending, or when the petition for extension of time or to revive in that application is granted, and when this application is granted a filing date, so as to make this application copending with said prior application.

NOTE: According to the Notice of May 13, 1983 (103, TMOG 6-7), the filing of a continuation or continuation-in- part application is a proper response with respect to a petition for extension of time or a petition to revive and should include the express abandonment of the prior application conditioned upon the granting of the petition and the granting of a filing date to the continuing application.

22. Petition for Suspension of Prosecution for the Time Necessary to File an Amendment

WARNING: *"The claims of a new application may be finally rejected in the first Office action in those situations where (A) the new application is a continuing application of, or a substitute for, an earlier application, and (B) all the claims of the new application (1) are drawn to the same invention claimed in the earlier application, and (2) would have been properly finally rejected on the grounds of art of record in the next Office action if they had been entered in the earlier application." M.P.E.P. Section 706.07(b), 7th ed.*

NOTE: Where it is possible that the claims on file will give rise to a first action final for this continuation application and for some reason an amendment cannot be filed promptly (e.g., experimental data is being gathered) it may be desirable to file a petition for suspension of prosecution for the time necessary.

(check the next item, if applicable)

[ ] There is provided herewith a Petition To Suspend Prosecution for the Time Necessary to File An Amendment (New Application Filed Concurrently)

23. Small Entity (37 C.F.R. Section 1.28(a))

[X] Applicant has established small entity status by the filing of a statement in parent application 09/119,187 filed on July 20, 1998.

[X] A copy of the statement previously filed is included.

WARNING: *See 37 C.F.R. Section 1.28(a).*

WARNING: *"Small entity status must not be established when the person or persons signing the . . . statement can **unequivocally** make the required self-certification."* M.P.E.P. Section 509.03, 7th ed. (emphasis added).

24. NOTIFICATION IN PARENT APPLICATION OF THIS FILING

[X] A notification of the filing of this
(check one of the following)

[ ] continuation

[ ] continuation-in-part

[X] divisional

is being filed in the parent application, from which this application claims priority under 35 U.S.C. Section 121.

Express Mail NO. EL564195246US

Express Mail Label No. EI768182393US

Attorney Docket No. 98-15

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(f) & 1.27(c)) – SMALL BUSINESS CONCERN

Applicant or Patentee: Christopher J. Warren, Robert C. Haushalter and Leonid Matsiev
Application or Patent No.: _____
Filed or Issued: Even Date Herewith
Title: COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND TESTING SYSTEM

I hereby declare that I am an official of the small business concern empowered to act on behalf of the concern identified below:

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I hereby declare that the above-identified small business concern qualifies as a small business concern as defined in 13 CFR 121.12, and reproduced in 37 CRF 1.9(d), for purposes of paying reduced fees to the United States Patent and Trademark Office, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare the rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND TESTING SYSTEM by inventors Christopher J. Warren, Robert C. Haushalter and Leonid Matsiev described in

[x] the specification filed herewith
[ ] Application No. _____, filed _____
[ ] Patent No. _____, issued _____

If the rights held by the above identified small business concern are not exclusive, each individual, concern or organization having rights in the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who would not qualify as an independent inventor under 37 CFR 1.9(c) if that person made the invention, or by any concern that would not qualify as a small business concern under CFR 1.9(d), or a nonprofit organization under 37 CFR 1.9(e).

*NOTE: Separate verified statements are required for each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

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Address: _____

[ ] Individual [x] Small Business Concern [ ] Nonprofit Organization

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b)).

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

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Express Mail No. EL564195246US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: Warren et al.

SERIAL NO.: GROUP NO.:

FILED: Herewith EXAMINER: To Be Assigned

TITLE: COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND TESTING SYSTEM

ATTORNEY DOCKET NO.: 1012-065D1 (98-15Div1)

PRELIMINARY AMENDMENT

Box Patent Application
Assistant Commissioner for Patents
Washington, DC 20231

Sir:

Prior to examination of the above-referenced application, please amend the application as follows:

IN THE CLAIMS

Please amend claims 30 and 32 as follows:.

30. (Amended) A system for electrochemically screening an array of materials, said system comprising:

(a) an array of different materials having an individually addressable electrode [for] corresponding to each different material in the array; and

(b) means associated with each of said electrodes for simultaneously testing each of said materials for [said specific material property] a common selected property.

32. (Amended) The system of claim 31, wherein said electrochemical cell comprises:

a cylindrical glass housing, said housing sandwiched between [two] end members and held in place with [at least four screw] fasteners;

a reference electrode compartment;

a liquid filling hole;

a cathode assembly; and

an anode array assembly, said anode array assembly holding said array of individually addressable electrodes.

CORRECTION OF INVENTORSHIP

In view of correction of inventorship being effected in the prior application, inventorship is being investigated in the present application. In the event correction is deemed necessary, Applicants will submit an appropriate request for correction.

REMARKS AND CONCLUSION

This is a divisional application of Serial No. 09/119, 187, filed July 20, 1998. Applicants have presented claims corresponding generally to Group V as set forth by the Examiner in the Restriction Requirement in that case.

It is believed that all of the claims are in form for allowance and such action is respectfully requested at the earliest possible time. If the Examiner has any questions regarding the present application, the Examiner is requested to contact the undersigned at (248) 593-9900.

If for some reason Applicants have not requested a sufficient extension and/or have not paid a sufficient fee for this response and/or for the extension necessary to prevent the abandonment of this application, please consider this as a request for an extension for the required time period and/or authorization to charge our Deposit Account No. 50-0496 for any fee which may be due.

Respectfully submitted,
DOBRUSIN DARDEN THENNISCH & LORENZ PLLC
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PATENT APPLICATION

for

COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND TESTING SYSTEM

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COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND TESTING SYSTEM

This application is a continuation-in-part of U.S. patent application 08/941,170 filed September 30, 1997, pending, the techniques of which are incorporated herein by reference for all purposes

FIELD OF THE INVENTION

The present invention relates to methods and apparatus for the electrodeposition of diverse materials. More specifically, the invention comprises a fully automated electrochemical deposition and testing system for the synthesis and parallel screening of distinct materials on arrays of individually addressable electrodes.

BACKGROUND OF THE INVENTION

Among the different techniques for the preparation of metal deposits, electrodeposition (also known as electroplating) is particularly attractive because of its relatively inexpensive instrumentation, low temperature operation, and simplicity. A further advantage of the technique is the relatively straightforward control of the thickness and composition of the depositing layers through electrical quantities such as current passed and potential applied.

Electroplating has been employed in small scale as well as industrial processes. For example, electroplating of precious metals to improve the appearance of an article or to create special effects is well known. Electroplating is also employed to improve the corrosion resistance of corrosive substances by depositing thin surface films of corrosion resistant metals such as zinc, tin, chromium, nickel and others. Wear resistant and friction modifying coatings of nickel, chromium, titanium and other metals and their

alloys are used to improve the wear resistance of bearing surfaces. Electroplating is also employed in the electronics industry to improve or modify the electrical properties of substrates such as contacts, printed circuits, electrical conductors, and other electrical items in which specific surface or surface-to-substrate conductive properties are desired. Distinct metals are often electroplated onto metal surfaces to improve soldering characteristics or to facilitate subsequent coating by painting or application of other adhering films such as plastics, adhesives, rubber, or other materials.

Although the electrodeposition of a single material has been extensively studied, the deposition of two or more metals by electrochemical methods is difficult because the conditions favorable for the deposition of one metal may differ substantially with those necessary for the deposition of the other. Factors including widely differing reduction potentials, internal redox reactions that can alter the oxidation states of the materials in solution, and species that are or become insoluble during the deposition can disrupt the process. Moreover, the nature of the electrodeposit itself is determined by many factors including the electrolyte composition, pH, temperature and agitation, the potential applied between the electrodes, and the current density. These issues are more prevalent as the complexity of the electrodeposit (and hence the number of species in solution) increases.

Complex electodeposited materials are desired in areas such as catalysis where the composition of the electrodeposit is critical to its catalytic activity. The discovery of new catalytic materials depends largely on the ability to synthesize and analyze new compounds. Given approximately 100 elements in the periodic table that can be used to make such catalysts, and the fact that ternary, quaternary and greater compositions are desired, an incredibly large number of possible compositions is generated. Taking each of the previously noted electrochemical issues into account for every possible electrodeposit and designing a synthetic strategy that can effectively cover phase space using traditional synthetic methodologies is a time consuming and laborious practice. As such, there exists a need in the art for a more efficient, economical, and systematic approach for the synthesis of novel materials and for the screening of such materials for useful properties. See, for example, copending U.S. patent application 08/327,513 entitled "The Combinatorial Synthesis of Novel Materials" (published as WO 96/11878).

As an example of the utility of exploring phase space for more effective catalysts, one can consider the effect of changing the composition of the anode in a direct methanol fuel cell. A tremendous amount of research in this area has concentrated on exploring the activity of surface modified binary, and to a much lesser extent ternary, alloys of platinum in an attempt to both increase the efficiency of and reduce the amount of precious metals in the anode part of the fuel cell. Although electrodeposition was explored as a route to the synthesis of anode materials (e.g., F. Richarz et al. *Surface Science*, **1995**, *335*, 361), only a few compositions were actually prepared, and these compositions were made using traditional single point electrodeposition techniques. Such an approach becomes very inefficient when exploring and optimizing new multi-component systems. Recently, Mallouk, et al. reported work on combinatorial electrochemistry as a route to fuel cell anode materials (*Science*, **1998**, *280*, 1735), but this technique did not employ electrodeposition techniques.

The present invention provides a method to use electrodeposition to synthesize and evaluate large numbers of distinct materials in relatively short periods of time, significantly reducing the time consuming and laborious processes normally associated with a novel materials discovery program.

SUMMARY OF THE INVENTION

This invention provides methods and apparatus for electrochemically depositing distinct materials on arrays of individually addressable electrodes. The invention also provides a means of testing the as deposited materials for specific properties of interest.

One embodiment of the invention includes the individually addressable electrode arrays and their associated fabrication and processing steps.

Another embodiment of the invention includes an automated deposition system comprising a solution delivery head and its associated electronics and robotics. The delivery head is capable of automatically dispensing precise mixtures of plating solutions to predefined locations above the working electrodes on the individually addressable electrode arrays. The head contains a reference and counter electrode, and while delivering the plating solutions completes a circuit with a given working electrode on the

array. Adjusting the potential applied to the working electrode on the array results in the deposition of materials from the delivered plating solutions.

Another embodiment of the invention includes an electrochemical testing system comprising an electrochemical cell, a multi-channel potentiostat, and an electronic interface designed to couple the addressable array to the potentiostat such that individual electrodes on the array may be addressed, either serially or in parallel, for the measurement of a specific material property under investigation.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to better understand the present invention, reference should be made to the following detailed description taken in conjunction with the accompanying drawings wherein:

FIG. 1A illustrates an array of 64 individually addressable electrodes made in accordance with the present invention;

FIG. 1B illustrates an array of 66 individually addressable electrodes made in accordance with the present invention;

FIG. 2A is a flow chart diagram describing the processes involved in fabricating individually addressable electrode arrays;

FIGS. 2A and 2B are examples of masks for array fabrication;

FIG. 3 is a sectional view of the electrochemical deposition head;

FIG. 4A is a sectional view of the electrochemical cell;

FIG. 4B is a sectional view of the cathode assembly associated with the electrochemical cell of FIG. 4A;

FIG. 4C is an exploded view of the anode assembly associated with the electrochemical cell of FIG. 4A;

FIG. 4D is a sectional view of the PCB interface associated with the anode assembly of FIG. 4C;

FIG. 4E is a circuit diagram showing the electrical connections in the PCB interface of Fig. 4D; and

FIG. 5 is a graph illustrative of the relationship between electrode composition and associated activity for an example system synthesized and measured using embodiments of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises an electrochemical synthesis and testing system consisting of a number of separate parts including individually addressable electrode arrays, a fully automated deposition head, an electrochemical cell and its associated electronics, and a multi-channel potentiostat. These components provide a means for investigating complex multi-component systems, by giving a user the ability to rapidly synthesize and evaluate large numbers of diverse materials in short periods of time.

The individually addressable electrode arrays 10 of the present invention are illustrated in FIGS. 1A and 1B. The arrays 10 consist of either sixty-four or sixty-six independent electrodes 12 (with areas of between 1 and 2 mm^2) that are fabricated on inert substrates 14. Arrays with as little as 10 or as many as 100 electrodes may be made in accordance with the methods provided in the present invention. Example substrates include, but are not limited to, glass, quartz, sapphire, alumina, plastics, or thermally treated silicon. Other suitable substrate materials will be readily apparent to those of skill in the art. The individual electrodes 12 are located substantially in the center of the substrate 14, and are connected to contact pads 13 around the periphery of the substrate with wires 16. The electrodes 12, associated wires 16, and contact pads 13 are fabricated from conducting materials (such as gold, silver, platinum, copper, or other commonly used electrode materials). In a preferred embodiment of the present invention, the arrays are fabricated on standard 3" thermally oxidized single crystal silicon wafers, and the electrodes are gold with surface areas of about 1.26mm^2.

Still referring to FIGS. 1A and 1B, a patterned insulating layer 18 covers the wires 16 and an inner portion of the peripheral contact pads 13, but leaves the electrodes and the outer portion of the peripheral contact pads exposed (preferably approximately half of the contract pad is covered with this insulating layer). Because of the insulating layer 18, it is possible to connect a lead (e.g., an alligator clip) to the outer portion of a

given contact pad and address its associated electrode while the array is immersed in solution, without having to worry about reactions that can occur on the wires or peripheral contact pads. The insulating layer may be, for example, glass, silica (SiO_2), alumina (Al_2O_3), magnesium oxide (MgO), silicon nitride (Si_3N_4), boron nitride (BN), yttrium oxide (Y_2O_3), titanium dioxide (TiO_2), hardened photoresist, or other suitable material known to be insulating in nature.

Once a suitable inert substrate is provided, photolithographic techniques can be applied to design and fabricate electrode array patterns on it. By applying a predetermined amount of photoresist to the substrate, photolyzing preselected regions of the photoresist, removing those regions that have been photolyzed (e.g., by using an appropriate developer), depositing one or more metals over the entire surface and removing predetermined regions of these metals (e.g., by dissolving the underlying photoresist), one can fabricate intricate patterns of individually addressable electrodes on the substrate.

The process by which the individually addressable electrode arrays of the present invention are fabricated is described with reference to the flow chart illustrated in FIG. 2A. Starting with a cleaning step 22 that comprises washing the wafer in a suitable solvent (such as methanol or isopropanol) followed by baking in a plasma cleaning oven, a photoresist deposition step 24 in which a first layer of photoresist is applied to the wafer is then done. Although many different types of photoresist can be used for the same effect, the preferred type in the present invention is Shipley Microposit S-1813 (or equivalent). The photoresist is applied to the wafer using a standard spin coating system (commonly used and familiar to those skilled in the art) which is set to leave a final thickness of between 1 and 2 μm on the wafer. The photoresist is then cured at a predetermined temperature for a predetermined time to condition the photoresist. In a preferred embodiment of the present invention, the curing temperature is between 90°C and 130°C and the curing time is between 30 sec and 2 minutes.

A primary electrode mask 27, an example of which is shown in Fig. 2B, (which is the negative of the electrode array pattern desired) is then placed over the wafer that is then photolyzed on a mask aligner system (commonly used and familiar to those skilled in the art). After exposure to ultraviolet (UV) light during the photolysis step 26, regions

29 on the wafer are then dissolved away using an appropriate developing solution (e.g., Shipley Microposit MF-319 or equivalent). The wafer is then placed in a physical vapor deposition (PVD) system where a metals are deposited during a metal deposition step 28. Example PVD systems include: sputtering, electron beam evaporation and pulsed laser deposition. The metals deposited by the appropriate PVD system consist of an adhesion layer (such as Cr, Ta, or W) followed by the desired electrode material (such as Au, Ag, Cu or Pt). The thicknesses of these layers may vary substantially, but are typically 100-500 Å for the adhesion layer and 1000-5000 Å for the electrode layer. Following a lift-off step 30 to remove the excess metals, a second layer of photoresist is then deposited on the wafer during a second photoresist deposition step 32, cured as described above, and photolyzed through an isolation mask 35 during a second photolysis step 34. The aim of this second photolysis step is to expose only the regions of the electrode pads 36 and an outer contact ring 38, the exposed photoresist on which is dissolved away after the photolysis step. A final annealing step 40 at between 90°C and 130°C for between 1 minute and 10 (or more) minutes hardens the remaining photoresist into an effective insulating layer. Alternately, an insulating layer (such as glass, silica, alumina, magnesium oxide, silicon nitride, boron nitride, yttrium oxide or titanium dioxide) may be deposited in place of the hardened photoresist by a suitable PVD technique after photolysis of the second photoresist layer through an inverse isolation mask (the negative of the isolation mask 35 in Fig. 2C).

The arrays of the present invention consist of a plurality of individually addressable electrodes that are insulated from each other (by adequate spacing) and from the substrate (since they are fabricated on an insulating substrate), and whose interconnects are insulated from the electrochemical testing solution (by the hardened photoresist or other suitable insulating material). The number of electrodes can vary according to a desired number, but typically the arrays consist of 10 or more electrodes, 30 or more electrodes, and preferably more than 50 electrodes. In the embodiments shown in Fig. 1A and Fig. 1B, more than 60 electrodes are in a single array. Materials are deposited on each of the individually addressable electrodes. Thus, an array of individually addressable materials is also a part of this invention, with the number of

materials equaling the number of addressable electrodes. The materials in the array may be the same or different, as described below.

The deposition of materials on the above described electrode arrays to make a library of an equal number of compositions is accomplished by the electrodeposition of species from solution using standard electrochemical methods. The compositions may all be the same, or may be different from each other. In one embodiment of the present invention, the depositions are carried out by immersing the electrode array in a standard electrochemical deposition chamber containing the array, a platinum mesh counter electrode, and a reference electrode (e.g., Ag/AgCl). The chamber is filled with a plating solution containing known amounts of source materials to be deposited. By selecting a given electrode and applying a predetermined potential for a predetermined amount of time, a particular composition of materials (which may or may not correspond to the exact composition of the plating solution) is deposited on the electrode surface. Variations in the compositions deposited may be obtained either by directly changing the solution composition for each deposition or by using different electrochemical deposition techniques, or both. Examples of how one may change the electrode composition by changing the deposition technique can include: changing the deposition potential, changing the length of the deposition time, varying the counter anions, using different concentrations of each species, and even using different electrochemical deposition programs (e.g., potentiostatic oxidation/reduction, galvanostatic oxidation/reduction, potential square-wave voltammetry, potential stair-step voltammetry, etc.). Through repeated deposition steps, a variety of materials may be serially deposited on the array for the aforementioned library.

In an alternate embodiment of the present invention, the deposition of materials on the electrode array is carried out using a partially or fully automated solution delivery/electroplating system consisting of a deposition head and its associated syringe pumps, robotics and electronics. As illustrated in Fig. 3, the deposition head 50 consists of a rod 52 that is tapered at the tip. The tapered end of the deposition head is wrapped with a mesh counter electrode 54 (e.g., Pt) that is connected to an external power supply (not shown) via a wire 56 that is embedded in the wall of the head. In a preferred embodiment of the present invention, the deposition head has a 1-3 mm ID which is

tapered to ca. 1 mm ID at the tip. A solution delivery tube 58 containing an interannular reference electrode 60 is located into the center of the rod 52. The reference electrode 60 may be a standard reference electrode (such as Ag/AgCl, SHE, SCE or $Hg/HgSO_4$) or a quasi-reference electrode (such as a piece of Pt wire). The reference electrode 60 is split off from the solution delivery tube 58 and connected to an external power supply or potentiostat (not shown). The flow of liquids through the solution delivery tube 58 is controlled by commercially available syringe pumps (not shown) that can precisely deliver volumes of liquids with accurate displacements in the μL/hour regime. Although any number of syringe pumps can be used, at least one is desirable and the exact number of pumps will ultimately depend on the complexity of the desired depositions (i.e., binary = two pumps, ternary = three pumps, quaternary = four pumps, etc.). The liquids that are dispensed from the aforementioned pumps are either mixed prior to entering the solution delivery tube (via an external mixer) or via a frit 62 embedded in the deposition head. During the deposition process, the deposition head 50 is held over a given electrode pad 12 on an electrode array 10 by a clamp 68 that is connected to robotics (not shown) that can control its precise position. In a preferred embodiment of the present invention, the ideal position, as illustrated in Fig. 3, is ca. 1-2 mm above the electrode pad 12.

Still referring to Fig. 3, the operation of the automated deposition system is described as follows. After positioning the deposition head above a given electrode (sometimes referred to as the 'working' electrode), the syringe pumps are activated causing a predetermined mixture of liquids containing predetermined amounts of source materials to flow through the tube 58 at an exactly specified flow rate and collect in a region 70 surrounding a given electrode 12. When the liquid contacts all three electrodes, a complete electric circuit is formed in this region. Coincident with the formation of this circuit, a predetermined potential is applied to the working electrode (via an external power supply or potentiostat) causing species present in the liquid above it to deposit on the electrode surface. After a predetermined deposition time, the head is rinsed and moved to the next electrode where the next specified mixture is delivered and plated out. In a preferred embodiment of the present invention, a deposition time of between 1 and 2 minutes is used. The entire procedure can take less than 3 minutes per deposition or about three hours per library of sixty-four to sixty-six elements.

The electrochemical cell used to measure properties of the materials deposited on the above described electrode arrays is illustrated in Figs. 4A-4E. Referring to Figs. 4A-4B, the cell 80 comprises a cylindrical glass housing 82 (of approximate diameter equal to that of the wafers) that is sandwiched between two plastic end members 84. The anode array assembly 86, which holds the individually addressable electrode arrays 10, is fit into one side of the cell, and the cathode assembly 95, which holds a counter electrode 88 and its associated external wire coupling 96, is fit into the other side. The cell is held together by four screw fasteners 90 which fit through holes 98 located on the corners of the end members 84. A reference electrode compartment 92 is bored into the glass housing to allow the insertion of a reference electrode (not shown). A liquid filling hole 94 allows for the filling and drainage of testing solutions from the electrochemical cell.

Referring to Fig. 4C, an exploded view of the components of the anode assembly is shown. The glass housing 82 of the cell is fit over the inner flange 106 of a molded adapter 102 and is held in place against the adapter with an o-ring 100. This o-ring provides a water-tight seal for this part of the assembly. The diameter of the outer flange 104 of the adapter 102 is the same as that of the glass housing, while that of the inner flange 106 is slightly smaller allowing one half of it to fit into the glass housing and the other half of it to fit into the remaining pieces of the anode assembly. A groove 108 is cut into the lower lip of the adapter 102. This groove holds an o-ring 110 which makes a water-tight seal with the anode array 10 when the adapter is pressed against it. Electrical contact to the anode array 10 is made using a ring of elastomeric contacts 114 which are pressed between the peripheral pads of the array (see Figs. 1A-1B) and contact pads 122 on a printed circuit board (PCB) assembly 112. These elastomeric contacts contain miniature wires encased in a flexible rubber sheath. They are commercially available and known to those skilled in the art. The anode array 10 is affixed to a backing plate 116 and attached to the PCB 112 with screws (not shown) through holes 118. This backing plate holds the electrode array and ensures contact between the peripheral pads on the wafer and the contacts on the PCB. This completes the anode assembly which is fitted together with screw fasteners 90 through holes 98 in end member 84 as shown in Fig. 4A.

Referring now to Figs. 4D-4E, the PCB 112 and its associated circuit diagram 130 are described as follows. The PCB 112 consists of a rectangular plate 120 on which is

deposited an intricate pattern of wires and connectors. The contact pads 122, which provide electrical connection to peripheral pads on the anode array (Figs. 1A-1B), are routed to four high-density pin connectors 128 that provide a cable connection to an external power supply (not shown) or multi-channel potentiostat 132. The multi-channel potentiostat 132 is essentially a collection of individual potentiostats bundled together in a single unit. These individual potentiostats can precisely control the current or potential applied to each electrode in the system. A common reference electrode contact 124 and a common counter electrode contact 126 are also wired to the high density pin connectors so that individual electrode pads on a given electrode array may be connected to the same reference and counter electrode during test measurements in the electrochemical cell.

Using the PCB 112 in conjunction with the deposition head 50 (Fig. 3) and the multi-channel potentiostat, each individual electrode on a given anode array can be individually addressed (e.g., during an electrodeposition procedure). Alternatively, using the PCB in connection with the electrochemical cell setup 80 (Fig. 4A) and multi-channel potentiostat, all of the electrodes on the array my be simultaneously addressed (e.g., during a catalytic activity measurement). Such catalytic measurements can be made in a time frame of between 1 and 2 minutes for each array of materials.

In the PCB illustrated in Fig. 4D, a sixty-four contact pad configuration is shown. It should be understood that a sixty-six contact pad configuration would be needed for experiments using a sixty-six member electrode array (Fig. 1B), and that PCB's having greater or less contact pads and associated connections are straightforward extensions of the concept and intended to be included within the scope of the present invention.

EXAMPLE

The following example illustrates the electrochemical deposition and screening measurements for a very specific system using selected embodiments of the present invention. It is only one of the many possible uses of the present invention. The example illustrates how a library of sixty-four different Pt-Ru compositions may be prepared and tested for methanol oxidation activity. It should be understood that the solution and

electrode compositions, types of reference and counter electrodes, applied and measured potentials, screening test conditions, and associated results are merely illustrative and that a person skilled in the art may make reasonable substitutions or modifications to these components without deviating from the spirit and scope of the invention.

A binary Pt-Ru library containing sixty-four different Pt-Ru compositions was synthesized on a sixty-four element individually addressable electrode array (gold electrodes) using the electrochemical reduction of acidic solutions containing mixtures of platinum chloride (H_2PtCl_6) and ruthenium chloride ($RuCl_3$). Starting with a stock solution of 150ml of 0.01M $RuCl_3$ (in 0.5M H_2SO_4) that was placed in a standard electrochemical deposition chamber along with the electrode array, a Pt mesh counter electrode, and a silver/silver chloride (Ag/AgCl) reference electrode, the first working electrode on the array was held at a constant potential of -0.25V (vs Ag/AgCl) for two minutes under constant stirring. The electrode array was then rotated in the deposition chamber and the solution composition adjusted (by the removal of a 5ml aliquot of the $RuCl_3$ solution and its replacement with a 5ml aliquot of a 0.01M H_2PtCl_6 solution), where the next electrode was deposited at the same potential and for the same amount of time. This procedure was continued until all sixty-four electrodes were deposited with Pt-Ru compositions, whose thickness averaged between 1000-2000 Å. Analysis (via X-ray fluorescence measurements) of the sixty-four electrodes showed a continuously varying gradient of Ru and Pt compositions among the sixty-four electrodes on the array.

This Pt-Ru library was then screened for methanol oxidation activity by placing it into the electrochemical cell (described earlier) which was filled with a solution of 1.0M methanol in 0.5M H_2SO_4 (a standard testing solution composition for studying the electrooxidation of methanol in fuel cells). The cell also contained a $Hg/HgSO_4$ reference electrode and a Pt mesh counter electrode. Chronoamperometry measurements (i.e., holding a given electrode at a given potential and measuring the current that passes as a function of time) were then performed on all of the electrodes in the library by pulsing each individual electrode to a potential of -0.125V (vs $Hg/HgSO_4$) and holding it

there for 1 minute while monitoring and recording the current that passed. The results of this experiment are depicted in Fig. 5.

Referring now to Fig. 5, a three-dimensional plot 140 of electrode composition 142 (expressed as mole fraction platinum) versus current 144 (in amps per square centimeter) versus time 146 (in seconds) is displayed. Individual electrodes are represented by their compositions along the x-axis, with their associated activities represented by their current values on the z-axis. The most active electrode compositions 150 are centered around a 50:50 Pt:Ru electrode composition which agrees with results reported in the literature (e.g., D. Chu and S. Gilman, *J. Electrochem. Soc.* **1996**, *143*, 1685). Although the results plotted in Fig. 5 correspond to a simple binary library of Pt-Ru compositions made by the serial deposition of Pt-Ru solutions in a standard deposition chamber and studied by serial chronoamperometry measurements made on a single channel potentiostat, the same depositions and measurements could be made in parallel with a multi-potentiostat using the deposition head and PCB interface of the present invention (Figs. 3 and 4D). In fact, significantly more complicated libraries using ternary, quaternary and greater compositions are possibly simply by changing the composition of the initial plating solutions. Plating solutions comprising one or more of the water soluble forms of the transition elements (e.g., Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg) as well as many main group elements (e.g., Al, Ga, Ge, In, Sn, Sb, Te, Tl, Pb, Bi) can be used with the present invention, and will give rise to enormous variations in library compositions which can in turn be studied in an enormous variety of catalytic systems.

As should now be readily apparent, the present invention provides a far superior method of electrochemically depositing and screening the properties of diverse materials. Using this invention, one can efficiently prepare libraries of varying elemental composition, and, since these libraries are prepared on individually addressable electrode arrays, one can also directly measure properties of these compositions. Using the present invention, it should be possible to synthesize and screen millions of new compositions at an unprecedented rate.

It is to be understood that the above description is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should, therefore, be determined not with reference to the above description, but should instead be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. The disclosures of all articles and references, including patent applications and publications, are incorporated herein by reference for all purposes.

What is claimed is:

1. A method of fabricating individually addressable electrode arrays, said method including the steps of:

providing an inert substrate;

applying photoresist to said substrate;

photolyzing preselected regions of said photoresist, said photolyzed regions being removable using a developer;

depositing one or more metals on said substrate;

removing predetermined regions of said metals, the remaining regions forming said array of individually addressable electrodes.

2. The method of claim 1, wherein said step of photolyzing preselected regions of said photoresist includes the steps of:

placing an electrode mask over said wafer; and

exposing said wafer to ultraviolet light.

3. The method of claim 1, wherein said step of depositing one or more metals on said substrate comprises the deposition of an adhesion layer followed by the deposition of an electrode layer.

4. The method of claim 3, wherein said deposition of said adhesion layer comprises depositing between about 100 and 500 Å of a metal selected from the group consisting of Cr, Ta and W.

5. The method of claim 3, wherein said deposition of said electrode layer comprises depositing between about 1000 and 5000 Å of a metal selected from the group consisting of Au, Ag, Cu and Pt.

6. The method of claim 1, further comprising the step of depositing an insulating coating on selected regions of said substrate.

7. The method of claim 6, wherein said step of depositing said insulating coating on selected regions of said substrate includes the steps of:

applying a second layer of photoresist to said inert substrate;

photolyzing preselected regions of said photoresist, the remaining regions being removable using a developer; and

annealing said substrate for a predetermined time at a predetermined temperature.

8. The method of claim 7, wherein said step of photolyzing preselected regions of said photoresist includes the steps of:

placing an isolation mask over said wafer; and

exposing said wafer to ultraviolet light.

9. The method of claim 7, wherein said step of annealing said substrate comprises heating said substrate at between about 90-130°C for between about 1-10 minutes.

10. An array of individually addressable electrodes on an inert substrate, said array consisting of:

a plurality of electrode pads;

a plurality of contact pads;

wires connecting said contact pads to said electrode pads; and

an insulating layer covering said wires and a predetermined portion of said contact pads.

11. The array of claim 10, wherein said electrode pads are located substantially in the center of said substrate and said contact pads are located around the peripheral edge of said substrate.

12. The array of claim 10, wherein said inert substrate is selected from the group consisting of glass, quartz, sapphire, alumina, plastic and thermally treated silicon.

13. The array of claim 10, wherein said insulating layer is selected from the group consisting of glass, silica, alumina, magnesium oxide, silicon nitride, boron nitride, yttrium oxide, titanium dioxide, and hardened photoresist.

14. The array of claim 10, wherein said electrode pads, said contact pads, and said wires are fabricated from conducting materials.

15. The array of claim 14, wherein said conducting materials are independently selected from the group consisting of gold, platinum, silver and copper.

16. The array of claim 10, wherein said plurality of electrode pads comprises at least 10 electrodes.

17. The array of claim 16, wherein said plurality of electrode pads comprises up to 100 electrodes.

18. The array of claim 10, wherein said electrode pads have a surface area of between 1 and 2 mm^2.

19. A method of depositing diverse materials on individually addressable electrode arrays, said method including the steps of:

providing an array of individually addressable electrodes, a power source, a reference electrode and a counter electrode;

delivering a mixture of source materials to predetermined locations on said array; and

depositing a predetermined composition of said source materials on a given electrode on said array.

20. The method of claim 19, wherein said step of delivering said mixture of said source materials includes the steps of:

positioning a deposition head over a given electrode on said array; and

activating a predetermined number of syringe pumps associated with said deposition head, said activation delivering a predetermined composition of said source materials to said predetermined locations on said array.

21. The method of claim 20, wherein said step of positioning said deposition head over said given electrode is accomplished using robotics.

22. The method of claim 21, wherein said robotics position said deposition head at a predetermined distance above said given electrode.

23. The method of claim 19 wherein said depositing step includes a step selected from the group consisting of changing the deposition potential, changing the length of the deposition time, varying the counter anions, using different concentrations of said source materials, and selecting the appropriate electrochemical deposition program.

24. The method of claim 23, wherein said electrochemical deposition program is selected from the group consisting of potentiostatic reduction, potentiostatic oxidation, galvanostatic reduction, galvanostatic oxidation, potential square-wave voltammetry, and potential stair-step voltammetry.

25. An apparatus for depositing diverse materials onto an array of individually addressable electrodes, said apparatus comprising:

a rod having a tapered end;

a solution delivery tube within said rod;

a reference electrode within said solution delivery tube;

a counter electrode attached to said rod;

means for controlling the composition and flow rate of liquids through said solution delivery tube;

means for mixing said liquids before said liquids exit said solution delivery tube; and

means for controlling the position of said apparatus over said array.

26. The apparatus of claim 25, wherein said means for controlling the composition and flow rate of said liquids through said solution delivery tube comprises at least one syringe pump.

27. The apparatus of claim 25, wherein said means for mixing said liquids before said liquids exit said solution delivery tube comprises an external mixer.

28. The apparatus of claim 25, wherein said means for mixing said liquids before said liquids exit said solution delivery tube comprises a frit, said frit embedded in said rod.

29. The apparatus of claim 25, wherein said means for controlling the position of said apparatus over said array comprises robotics.

30. A system for electrochemically screening an array of materials, said system comprising:

an array of materials having an individually addressable electrode for each material in the array; and

means associated with each of said electrodes for simultaneously testing each of said materials for said specific material property.

31. The system of claim 30, wherein said means comprises an electrochemical cell, a multi-channel potentiostat, and a printed circuit board assembly.

32. The system of claim 31, wherein said electrochemical cell comprises:

a cylindrical glass housing, said housing sandwiched between two end members and held in place with at least four screw fasteners;

a reference electrode compartment;

a liquid filling hole;

a cathode assembly; and

an anode array assembly, said anode array assembly holding said array of individually addressable electrodes.

33. The system of claim 32, wherein said anode array assembly comprises:

a first o-ring, said first o-ring forming a water-tight seal with said glass housing;

a molded adapter having an inner flange, an outer flange, and at least one groove;

an array of individually addressable electrodes;

a second o-ring, said second o-ring fitting into said groove and forming a water-tight seal with said array of individually addressable electrodes;

a printed circuit board;

a ring of elastomeric contacts, said elastomeric contacts located between said array and said printed circuit board; and

a backing plate.

34. The system of claim 33, wherein said printed circuit board comprises:

a predetermined number of contact pads, said number of contact pads corresponding to the number of individually addressable electrodes on said array;

at least four high density pin connectors;

a common reference electrode contact; and

a common counter electrode contact.

35. A method of testing a specific property of a material, said method including the steps of:

depositing distinct materials on an array of individually addressable electrodes;

placing said array in an electrochemical cell; and

screening said array for said specific property.

36. The method of claim 35, wherein said screening comprises:

pulsing all of said electrodes on said array to a predetermined potential and monitoring and recording the current that is passed.

37. The method of claim 35, wherein said specific property for said array is screened in a time frame of less than 5 minutes.

ABSTRACT OF THE DISCLOSURE

An electrochemical deposition and testing system consisting of individually addressable electrode arrays, a fully automated deposition head, and a parallel screening apparatus is described. The system is capable of synthesizing and screening millions of new compositions at an unprecedented rate.

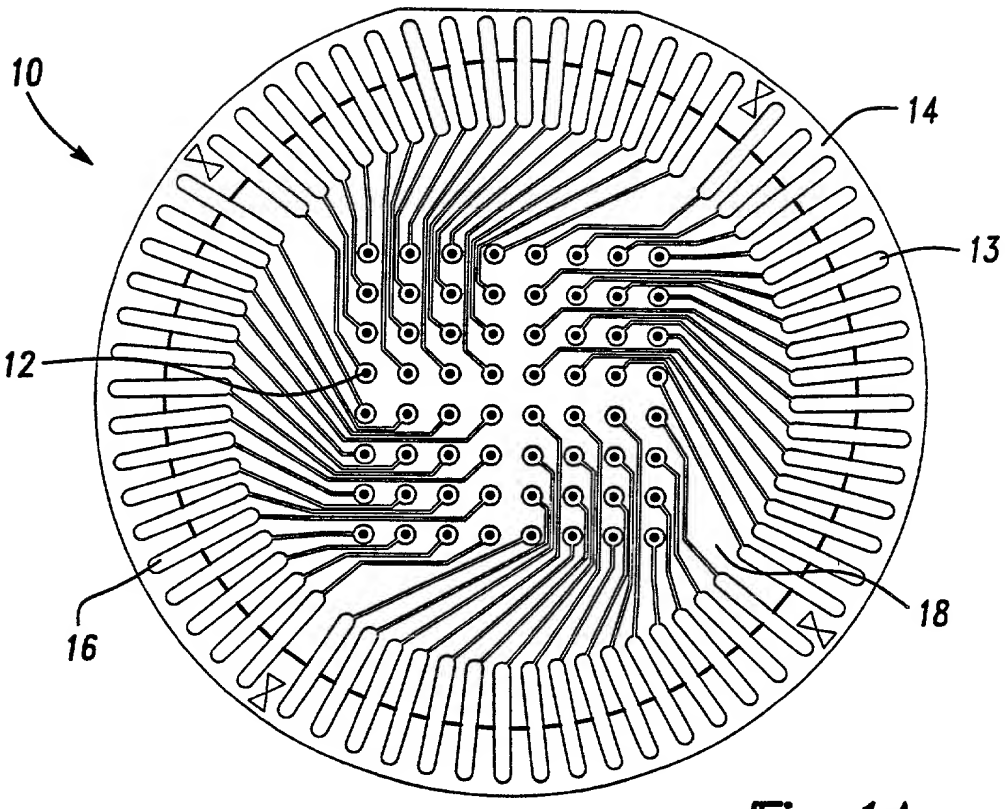


Fig-1A

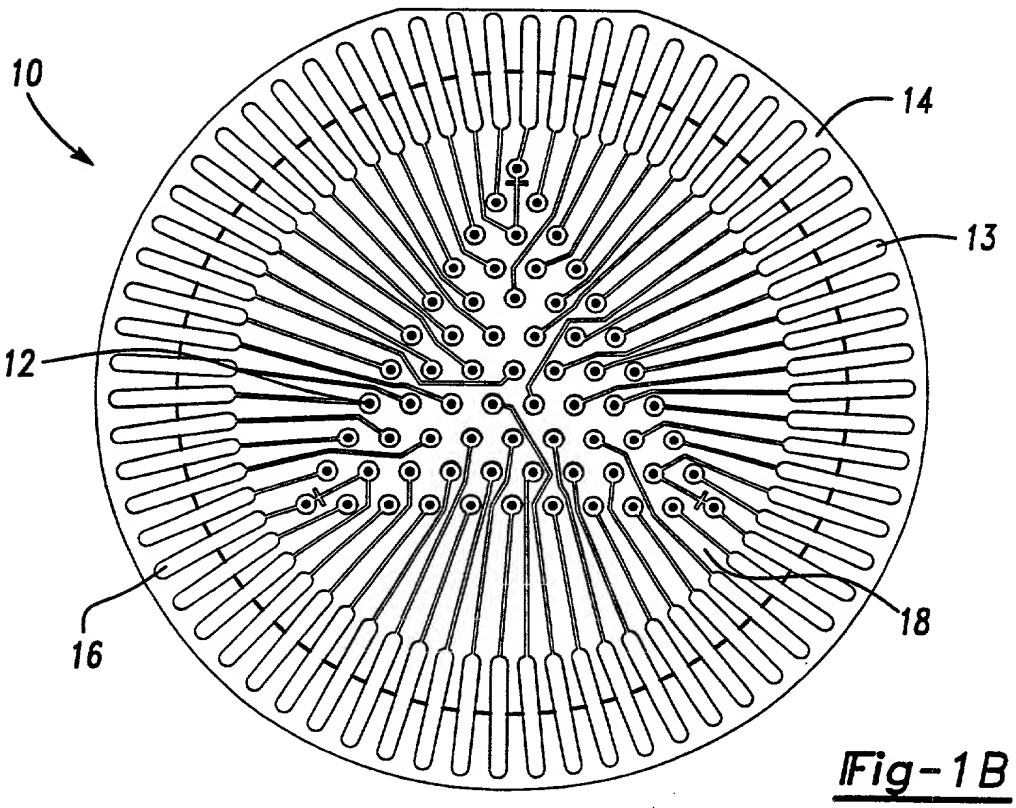


Fig-1B

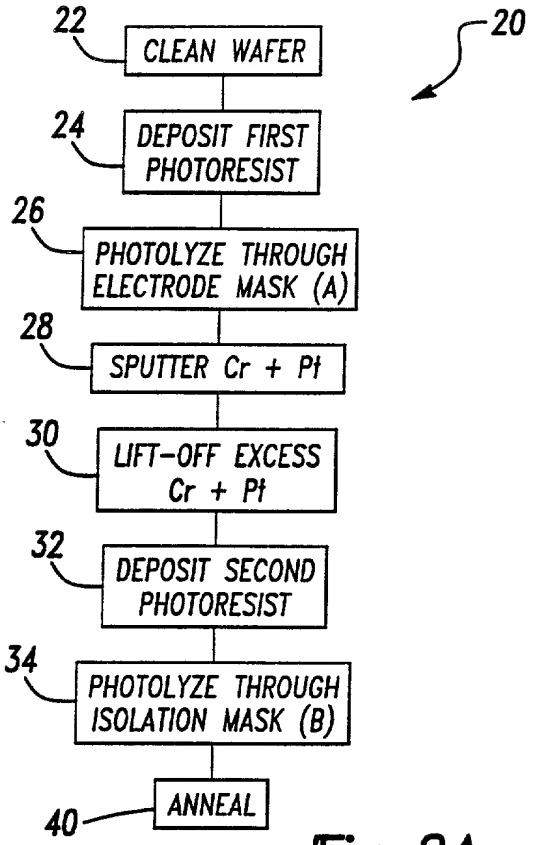


Fig-2A

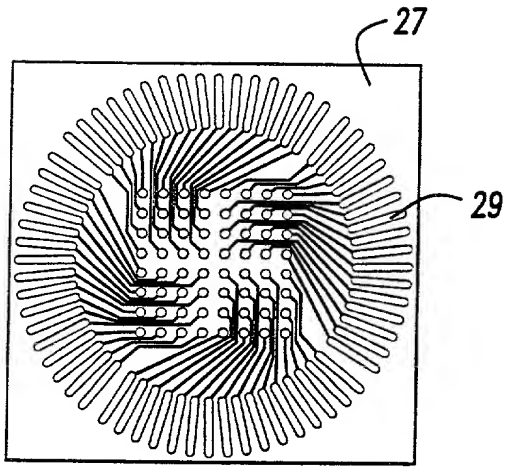


Fig-2B

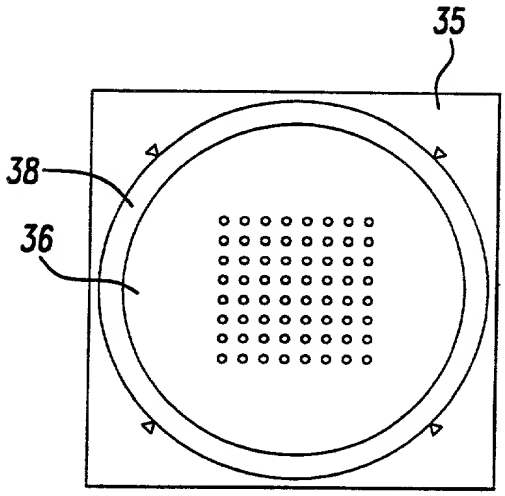


Fig-2C

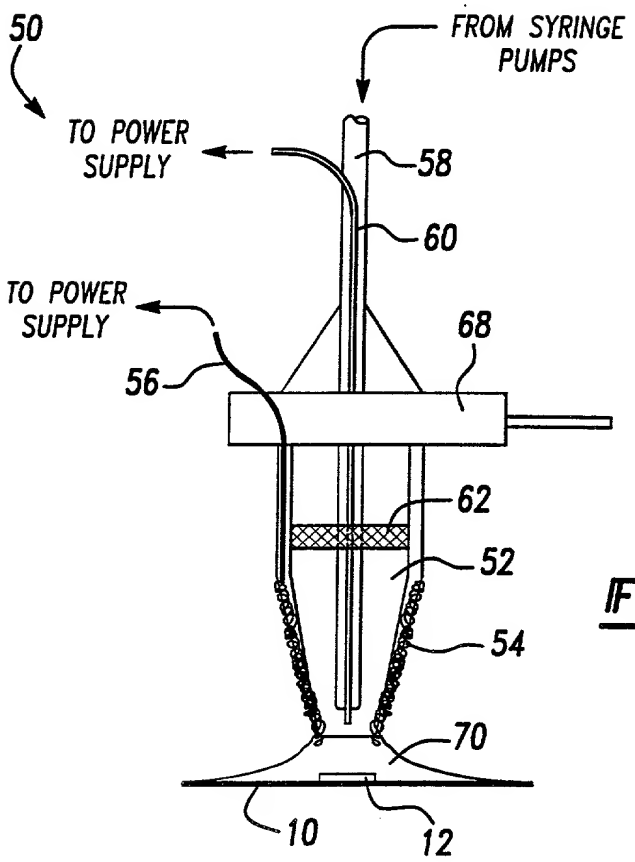
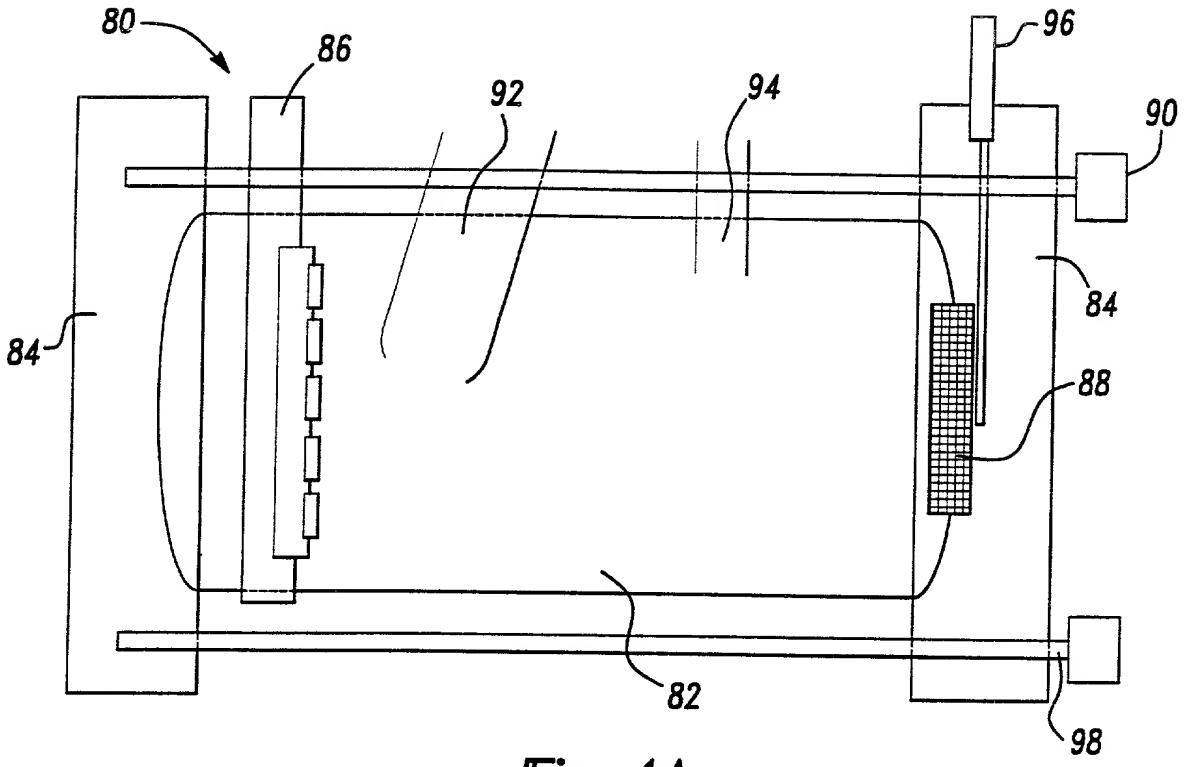


Fig-3



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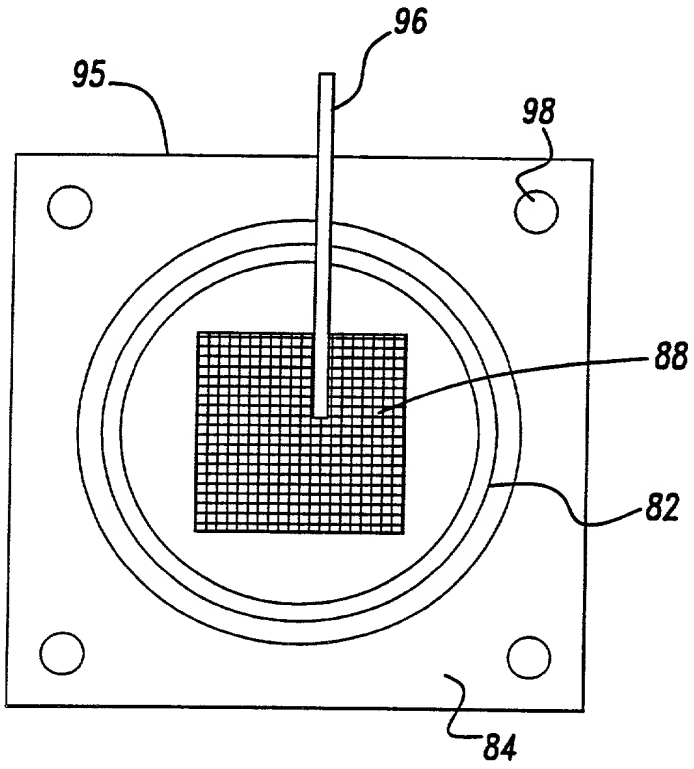

Fig-4B

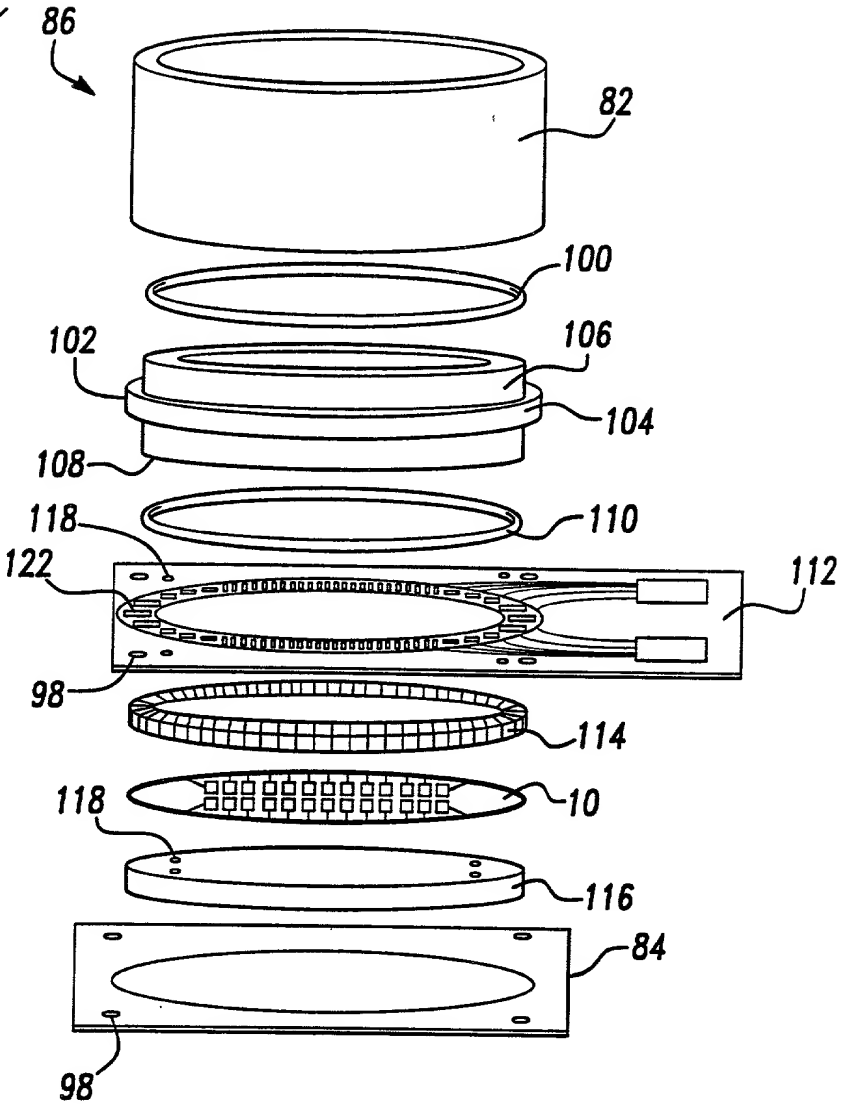
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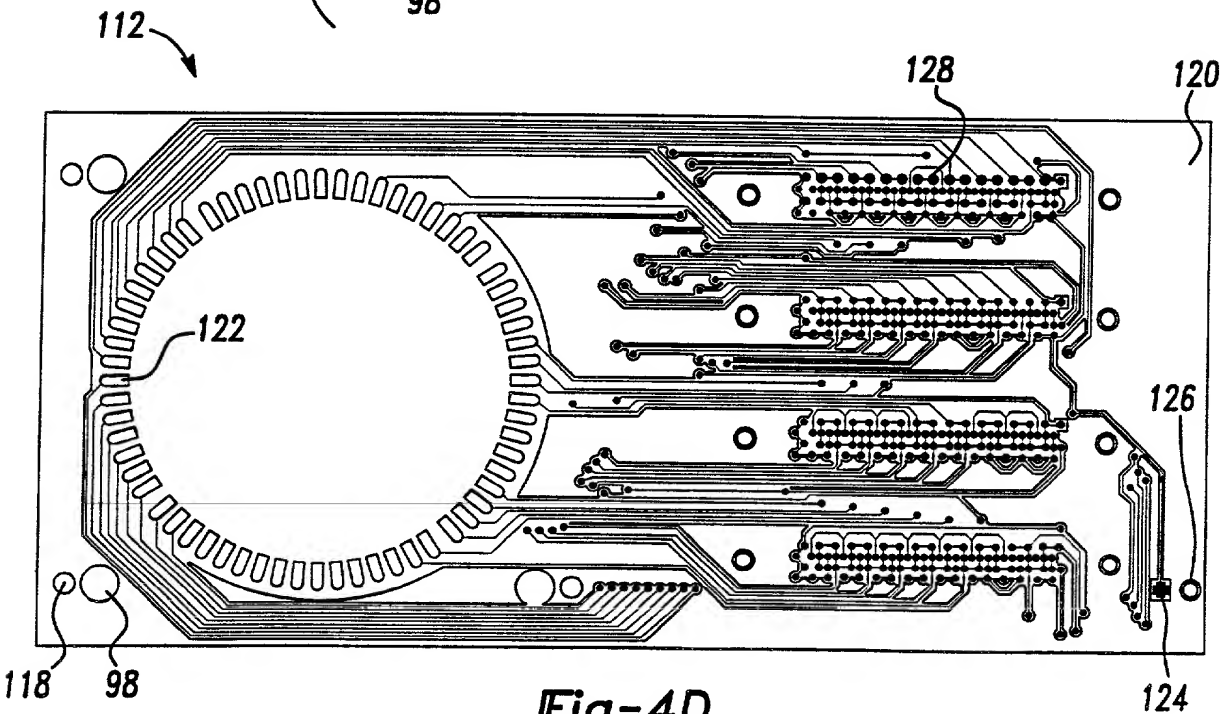
Fig-4C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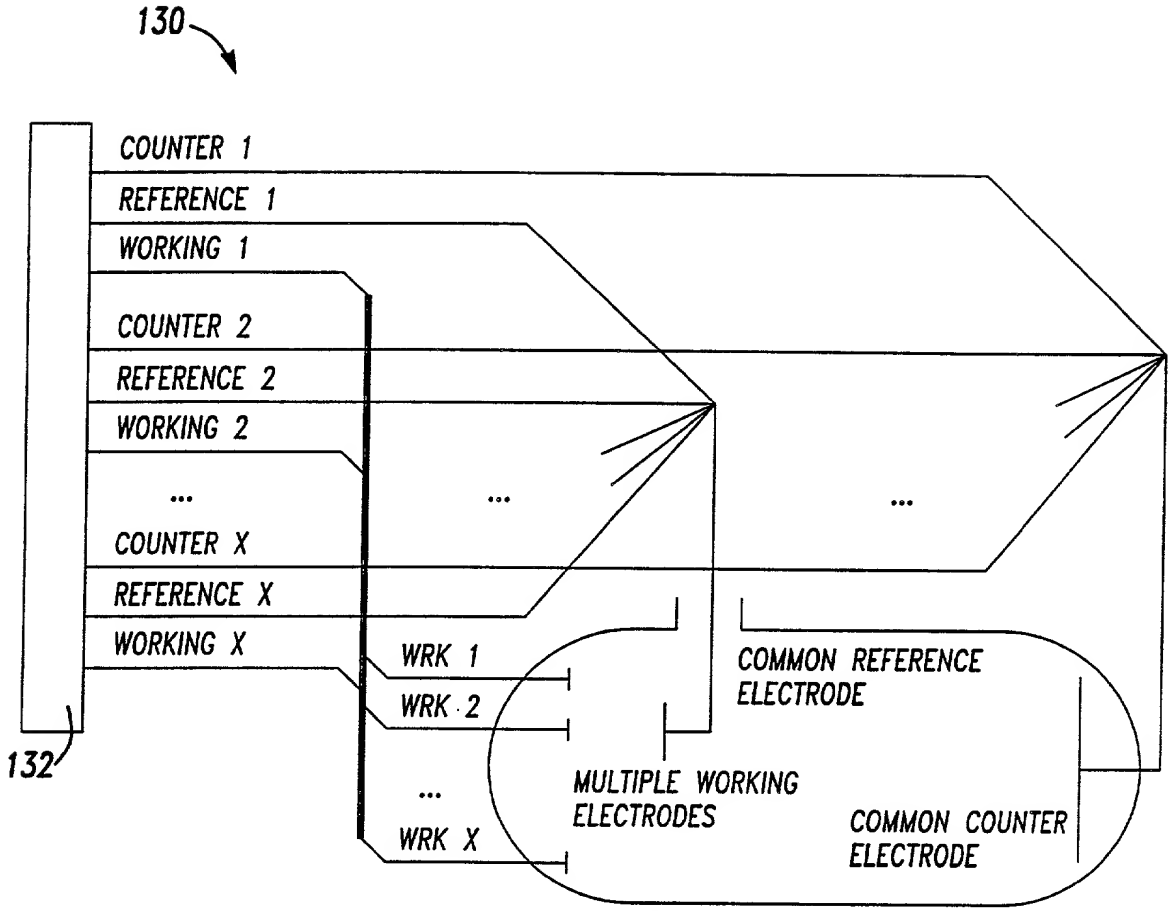
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Fig-4E

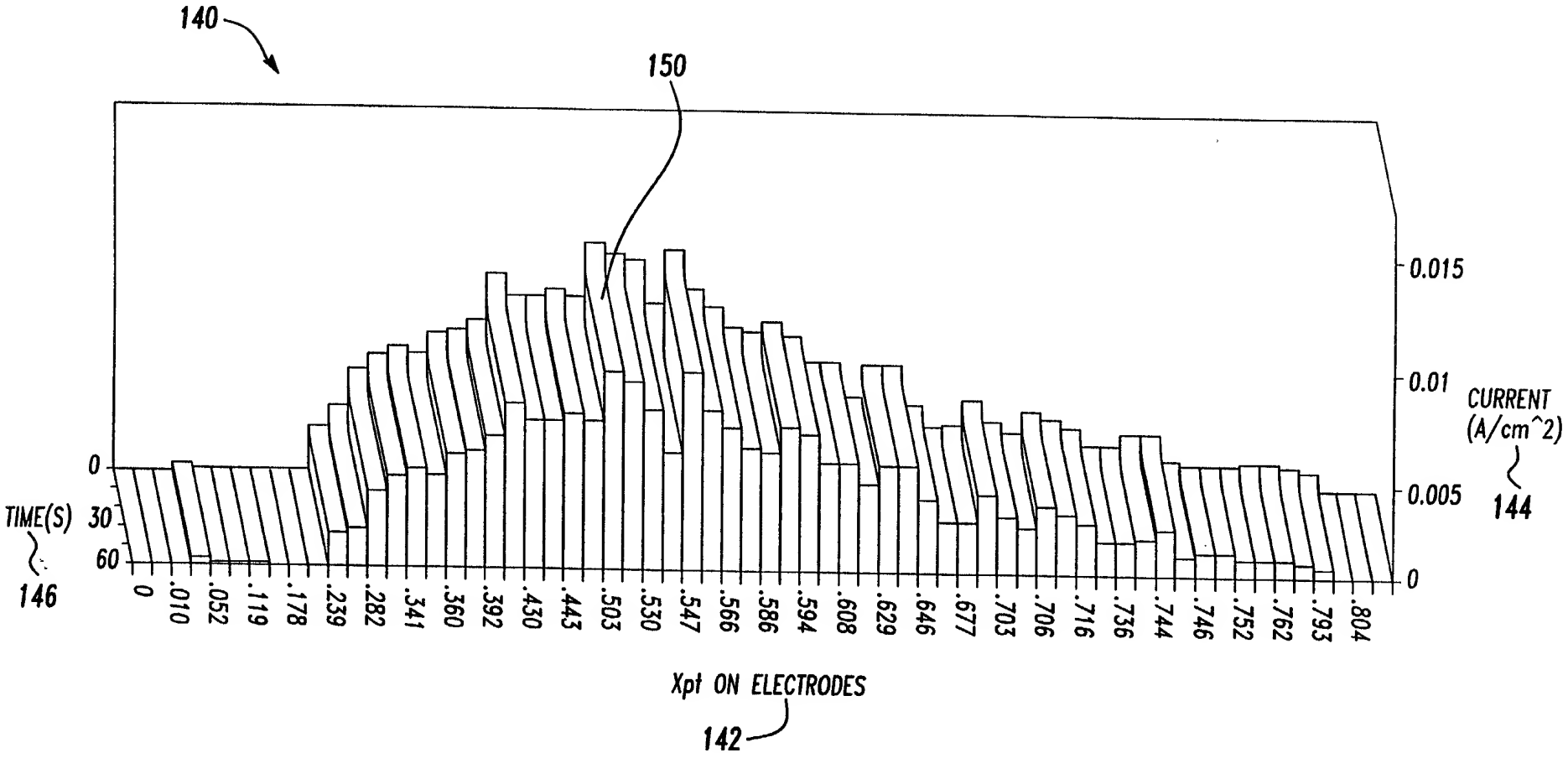

Fig-5

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Express Mail Label No. EI768182393US

Attorney Docket No. 98-15

DECLARATION

As a below and named inventor, I declare that:

My residence, post office address and citizenship are as stated below next to my name; I believe I am the original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled: COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND TESTING SYSTEM the specification of which x is attached hereto or ___ was filed on _____ as Application No. _____ and was amended on _____ (if applicable).

I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56. I claim foreign priority benefits under Title 35, United States Code, Section 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Country	Application No.	Date of Filing	Priority Claimed Under 35 USC 119
			Yes____ No____
			Yes____ No____

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below:

Application No.	Filing Date

I claim the benefit under Title 35, United States Code, Section 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Section 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, Section 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Application No.	Date of Filing	Status
08/941,170	September 30, 1997	__ Patented x Pending __ Abandoned
		__ Patented __ Pending __ Abandoned

Power of Attorney: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

Ronald A. Krasnow, Reg. No. 33,321

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I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signature of Inventor 1	Signature of Inventor 2	Signature of Inventor 3
Christopher J. Warren	**Robert C. Haushalter**	**Leonid Matsiev**
Date 7/16/98	Date 7/20/98	Date 07.16.98

Express Mail NO. EL564195246US

Attorney Docket No. 1012-065 (98-15)

ASSOCIATE POWER OF ATTORNEY BY ASSIGNEE

SYMYX TECHNOLOGIES, INC. is the Assignee of the invention entitled:

COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND TESTING SYSTEM

_____ the specification of which ____ is attached hereto or ___ was filed on July 20, 1998 as Application Serial No. 09/119,187.

Assignee hereby appoints the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

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Loletta L. Darden (Reg. No. 37,603)
Paul A. Stone (Reg. No. 38,628)

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SYMYX TECHNOLOGIES, INC.

Date: Jan. 28, 2000

By: Ronald A. Krasnow
(signature)

Name: Ronald A. Krasnow
Title: VP & CPC

United States Patent & Trademark Office

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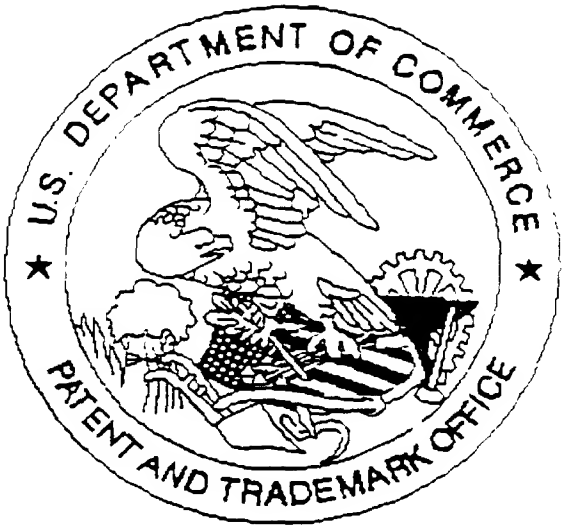

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